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Coal oil fuel.

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A coal oil fuel contains asphaltenes separated from vis-
broken fuel oil. Preferably the oil component is not vis-broken.
Stability is improved without excessive increases in viscosity.

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COAL OIL FUEL

The present invention relates to coal oil fuels.

Coal oil fuels are pumpable materials which contain coal particles suspended in an oil.

Coal oil fuels may be the so-called coal oil mixtures (COM) which are dispersions of powdered coal of relatively large particle size in an oil. These often require the presence of a surfactant to provide adequate stability. Coal oil fuels may also take the form of the so-called coal oil dispersion (COD) in which the coal particle size is considerably finer and which do not usually require the use of added surfactants to obtain a satisfactory storage stability.

It is disclosed in US 2 231 513 that coal oil fuels may be made from inter alia visbroken fuel oil. There is no suggestion however than any specific component in the visbroken fuel oil gives any advantage in improving the stability of the resulting fuel.

It is disclosed in Japanese unexamined published patent specification 57-98595 that asphaltenes may be added to dispersions of coal powder in a liquid oil. The asphaltene may be obtained from crude oil.

We have now found that the source of the asphaltene is very important if a useful improvement in the stability against settling of a coal oil fuel is to be obtained.

According to the present invention a coal oil fuel comprising coal particles suspended in oil is characterised in that it contains asphaltenes separated from visbroken fuel oil.

Coal oil fuels are well known materials and the skilled reader

will be readily able to make coal oil fuels suitable for incorporation of asphaltenes in accordance with the present invention.

The coal oil fuels which are known as coal oil mixtures (COM) are in general made from the product known as "pulverised coal".

5 "Pulverised coal" is the ground coal usually supplied for large coal burning furnaces in for example power stations. Examples of typical particle sizes for such material are 80% by weight through a 200 mesh sieve or 80% by weight less than 75 microns. Coal oil mixtures may be made by agitating the coal particles and the oil together under
10 relatively low shear conditions as is well known to those skilled in making coal oil mixtures.

Where the coal oil fuel is a coal oil dispersion (COD) the coal particles will be much finer. Examples of preferred coal particle sizes are for example those having an average particle size between 1
15 and 10 microns. The method of making coal oil dispersions is important if optimum stability is to be obtained. Preferred methods of making coal oil dispersions are disclosed in GB 1 523 193.

The quantity of coal present may vary over a moderately wide range eg 30 - 50% wt coal based on total weight of coal oil fuel.

20 The oils which may be used to make the coal oil fuel may be any combustible non-water miscible liquid. Vegetable oils may be used, as can oils derived from coal. In general petroleum and its fractionation products are preferred. The preferred oils are fuel oils. Fuel oils are derived from residues from petroleum distillation or cracking. The viscosity is usually not more than 600 mm²/sec
25 (600 cSt) at 50°C, preferably not more than 380 cSt at 50°C. The required viscosity may be achieved by diluting (otherwise known as "cutting back") with a less viscous material eg gas oil or kerosene. The oil is preferably a non-vis broken fuel oil, and may for example
30 be a straight run fuel oil ie a fuel oil obtained directly by distillation of crude petroleum.

Asphaltenes are high molecular weight materials found in crude petroleum and in residual materials resulting from the distillation of crude petroleum. They are insoluble in lower molecular weight
35 aliphatic hydrocarbons such as heptane and are precipitated out when

heptane is added to a material such as crude petroleum or fuel oil in which the asphaltenes are dissolved.

Asphaltenes are often considered to be undesirable in liquid petroleum derived products such as fuel oils. They may be removed from such materials by the solvent deasphalting process. In this process a relatively low boiling aliphatic solvent eg octane, heptane or pentane is added to the liquid to be deasphalted causing the asphaltenes to precipitate out. The asphaltenes may be recovered by centrifuging.

The asphaltenes used in the process of the present invention are those obtained from a vis-broken fuel oil. The process of "vis-breaking" is a well known refinery process in which residue from crude oil distillation is subjected to a mild thermal cracking operation to break down some of the high boiling compounds into lower boiling, less viscous compounds thereby reducing the viscosity of the resulting product. This process must be distinguished from more severe cracking processes which are intended to convert the fuel oil into other products.

The quantity of asphaltene used may for example vary between 0.5 and 10% based on total weight of coal and oil, preferably 1 to 3%.

High viscosities are undesirable as it becomes more difficult to handle the coal oil fuel.

In the case of coal oil dispersions the viscosity of the coal oil dispersion containing asphaltenes is preferably not more than 2.5 Pa.s at 80°C, preferably not more than 2 Pa.s at 80°C. (The viscosity may be determined with a Brookfield viscometer at 12 rpm).

In order to meet these preferred viscosity limits, restrictions are necessary on the quantity of asphaltenes added. In addition a restriction on the oils which can be used is involved, and in particular it is necessary to avoid the use of vis broken fuel oils as can be seen from the experiments set out below, if products containing a useful amount of coal are to be obtained without excessively high viscosities.

The invention will now be described with reference to the following examples.

Comparative Test A

A coal oil mixture was prepared from coal from the Herrington Colliery (NCB Rank 401) and from a commercially available fuel oil. The coal was in the form of pulverised coal and had a particle size distribution as follows:

Table A

Herrington Particle size distribution
Pulverised fuel size - Comparative Test A

	Diameter (μm)	Cumulative weight % oversize
10	125	1.7
	90	5.3
	45	36.8
	25	61.2
15	20	68.0
	15	74.9
	10	82.6
	5	91.5
	1	100

The fuel oil ex BP Oil Kent Refinery Limited had the following characteristics:

Table B

	Relative Density at 15.6/15.6°C	0.9870
	Sulphur (%wt)	2.80
25	Kinematic viscosity at 60°C (cSt)	289
	80°C (cSt)	101
	100°C (cSt)	45.9
	Wax content (%wt)	6.0
	Carbon Residue (%wt)	12.5
30	Asphaltenes (%wt)	3.4
	Asphaltum (%wt)	8.0
	Xylene Equivalent	11/15

The coal oil mixture was prepared as follows: 100 g of coal was stirred into 100 g of fuel oil at 70°C using a high speed mixer.

Mixing was continued for 5 minutes to ensure complete dispersal of the

coal. The stability of the resulting coal oil mixture was determined by the BP Stability Test. This is described on page 3 of the paper "Stable Coal/Fuel Oil Dispersions" presented at the second International Symposium of Coal Oil Mixture Combustion, Danvers, Massachusetts, USA, 27-29 November 1979 by Veal et al.

This involves determining the concentration of solids present at the base of the standard tube kept at 100°C for 24 hours and subtracting from it the initial concentration of solids in the dispersion. Clearly, the greater the difference the more the solids have separated and the more unstable is the dispersion.

When no asphaltenes are added to the fuel oil used to make coal oil mixture the value from the stability test was 12.0%.

Comparative Test B

In another comparative test carried out as in the preceding test, a coal oil mixture was prepared using the same fuel oil to which was added 2% by weight, calculated on the total weight of coal and fuel oil, of asphaltenes separated from the fuel oil used.

The result obtained in the stability test was 11.6% wt. The fuel oil used was not prepared using a vis-breaking process and this showed that the addition of asphaltenes from non vis-broken fuel oil has very little effect on the stability of the resulting coal oil mixture.

Example 1

Coal oil mixture was prepared as in the previous experiment but using asphaltenes derived from a visbroken fuel oil (see Table C). The result obtained in the stability test was 2.1% wt. As the figure given by the stability test should be as low as possible for maximum stability, this shows that the use of asphaltenes from visbroken fuel oil gives very substantial, and unexpected improvements in the stability of coal oil mixtures.

Examples 2-4

This example shows the preparation of a coal oil dispersion (COD). The coal used was from the Herrington, UK, colliery and was in pulverised form ie it corresponded to the coal used to prepare the coal oil mixture of Example 1. It was mixed with heptane to form a slurry and was ground in a KDL Pilot Dyno stirred ball mill

manufactured by Willy A Bachofen Maschinefabrik, Basle, Switzerland. The heptane was allowed to evaporate in air in a current of nitrogen to produce a quantity of finely divided coal. The average particle size was known from previous experience to be between 1 and 10 microns diameter.

40 grams of this coal powder was added to weight aliquots of the same non-visbroken fuel oil as was used in Example 1, to which known weights of asphaltene material had been added.

The asphaltene material used was precipitated using an excess of heptane, from a visbroken fuel oil having the following characteristics:

Table C

	Relative Density at 15.6/15.6°C	0.9900
	Sulphur (Zwt)	1.79
15	Kinematic viscosity at 60°C (cSt)	295
	80°C (cSt)	99
	100°C (cSt)	43
	Wax content (Zwt)	9.5
	Carbon Residue (Zwt)	16
20	Asphaltenes (Zwt)	7.0
	Asphaltum (Zwt)	4.3
	Xylene Equivalent	56/60

The mixture of coal, fuel oil and asphaltenes were stirred for 10 minutes using a high speed stirrer.

The stability was measured using the BP stability test. The viscosity was measured using a Brookfield viscometer. The quantities of materials used and the results obtained are given in Table 1.

Comparative Test C

An experiment was carried out as in Example 2 but without adding any asphaltenes. The quantities used and results obtained are shown in Table 1.

Comparative Test D

An experiment was carried out as in Example 2 using a visbroken fuel oil. This was the same visbroken fuel oil as was used as a source of asphaltenes in Example 1. This visbroken fuel oil contained

a large proportion of asphaltenes such that the COD containing 40% coal contained 4.2% of asphaltenes. However no asphaltenes were added to the fuel oil. The quantities used and the results obtained are shown in Table D.

Table D

Experiment	wt % fuel oil	wt % asphaltenes added	% wt coal	Stability Test (1)	Viscosity 80°C x 10 ⁻³ Pa.S (2)
C	60	0	40	10.3	1000
2	59	1	40	2.2	1400
3	58	2	40	0	1620
4	57	3	40	0.6	2360
D	60	0	40	1.5	3000
E	59.2	0.8	40	8.6	-
F	58	2.0	40	2.3	-

(1) Increase in base coal content at 100°C

(2) Measured with a Brookfield viscometer at 12 rpm.

Comparative Tests E and F

An experiment was carried out as in Example 2 but using asphaltenes from another sample of the non-visbroken fuel oil used in Example 1.

The results are shown in Table D.

Comparative Test G

40 g of finely divided Herrington coal powder (average size between 1 and 10 microns diameter) was stirred into a commercial fuel oil (820Z see Table E) for 10 minutes using a high speed stirrer as before (Example 2). The stability was measured using the BP stability test and showed an increase in base coal content of 16.9% wt.

Example 5

Mixtures of coal and oil were then prepared as in Test G but containing 1% and 2% wt of asphaltene material precipitated from the visbroken oil (Table C). These mixtures showed increased in base coal content of 6.9% and 1.6% by weight respectively (see Table F).

Comparative Test H

Similar mixtures containing 1 and 2% wt of asphaltene material

precipitated from a non-visbroken oil (Table B) showed increases in base coal contents of 13.4% and 5.9% by weight respectively.

Table E

F80 820Z Fuel Oil Analysis

5	Relative Density at 15.6/15.6	0.9845
	Sulphur (%wt)	3.61
	Kinematic viscosity at 60°C (cSt)	228
	80°C (cSt)	86.9
	100°C (cSt)	40.2
10	Wax content (%wt)	3.9
	Carbon Residue (%wt)	13.0
	Asphaltenes (%wt)	3.1
	Asphaltum (%wt)	17.5

Table F

15	Expt.	wt % fuel oil	wt % asphaltenes added	% wt coal	Stability Test
	G	60	0	40	16.9
	5	59	1	40	6.9
		58	2	40	1.6
20	H	59	1	40	13.4
		58	2	40	5.9

Discussions of Experimental Results

A comparison of the results for Example 2 and Test E and Example 3 and Test F shows that asphaltenes recovered from visbroken fuel oil give a greater increase in stability ie lower stability test values, than asphaltenes from non-visbroken fuel oil.

A comparison of Examples 2, 3 and 4 with Test D shows that the use of asphaltenes from visbroken fuel oil in a non-visbroken fuel oil enables high levels of stability to be obtained with lower product viscosity than possible using visbroken fuel oil. The lower viscosity is of course desirable as it aids pumping.

Claims:

1. A coal oil fuel comprising coal particles suspended in oil is characterised in that it contains asphaltenes separated from vis broken fuel oil.
2. A coal oil fuel according to claim 1 characterised in that it is
5 a coal oil dispersion.
3. A coal oil fuel according to either of claims 1 and 2 wherein the oil in which the particles are suspended is fuel oil.
4. A coal oil fuel according to claim 3 wherein the fuel oil is a non-vis broken fuel oil.
- 10 5. A coal oil fuel according to any one of the preceding claims wherein the quantity of asphaltenes derived from vis broken fuel oil is 0.5 to 10% by weight based on total weight of coal and oil.
6. A coal oil fuel according to claim 5 wherein the quantity of asphaltenes is in the range 1 to 3% by weight.
- 15 7. A coal-oil dispersion according to any one of the preceding claims having a viscosity of not more than 2.5 Pa.s measured at 80°C.
8. A coal-oil dispersion according to claim 7 wherein the coal-oil dispersion has a viscosity of not more than 2 Pa.s.

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EUROPEAN SEARCH REPORT

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Application number

EP 84 30 3172

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
A	GB-A- 165 423 (BATES) * Claims 1-3; page 2, lines 10-29 * -----	1-4	C 10 L 1/32
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 10 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24-07-1984	Examiner DE HERDT O.C.E.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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